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MATERIALS SELECTION AND PERFORMANCE IN GAS TURBINES FOR BASE LOADED UTILITY ELECTRICAL GENERATION

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ABSTRACT

Gas turbine driven electrical generating units are currently available with output in the 100 to 150 MW range. Low installed cost and short lead time have traditionally favoured such units. However, conventional operation involving use of expensive gaseous or distillate fuels and low thermal recovery has normally limited their use to short term peaking applications. Development of advanced coal gasification technology promises an abundant supply of relatively inexpensive clean fuel. When burned in a combined cycle plant in which the formerly wasted gas turbine exhaust heat is largely recovered for steam turbine propulsion, unit efficiencies are greater than those achieved in conventionally fossil fuel fired boiler operations. Although similar in many important respects to aircraft propulsion units, significant differences in component sizing, operating mode, mass considerations and life expectancy often dictate an alternative approach to materials selection. This report presents both a current state-of-the-art review of existing practice and a forward looking approach toward future materials development and application.

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EXECUTIVE SUMMARY

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The use of expensive gaseous or distillate fuels in gas turbines has been justifiable over the past several decades for provision of electrical utility peak demands. Recent advances in coal gasification technology and development of the combined cycle philosophy have increased overall unit efficiency beyond that achieved in conventional fossil fired boiler steam turbine plants. This together with short lead time requirements and lower installation costs increase the attractiveness of gas turbines for possible base loaded duties. For a life expectancy in excess of 100,000 hours, careful attention must be paid to turbine component materials selection and performance. Although some aircraft engine technology is applicable, large land based gas turbines with output in the 100 to 150 MW range have many unique characteristics and requirements. This report presents the rationale for current practice in materials selection together with the direction of research efforts toward more advanced alternatives.

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To: Dr. D. Mills
Director of Research

MATERIALS SELECTION AND PERFORMANCE IN GAS TURBINES FOR BASE LOADED ELECTRICAL UTILITY GENERATION

1.0 *INTRODUCTION*

Anticipation of the possible introduction of large (ie. 100 to 150 MW) base loaded gas turbine powered generation into the Ontario Hydro system prompted this review of current materials selection and operating experience. Also of interest are established and developing repair philosophies and the direction of research activities into improved performance, efficiency and reliability. The most probable scenario sees the introduction of turbines which will initially burn natural gas and not incorporate the superior efficiencies associated with exhaust heat recovery in a steam generating combined cycle plant. Later it is envisioned that a modern coal gasification plant will supply a clean gaseous fuel of low to medium calorific value to combined cycle units.

Gas turbine materials selection varies depending on the stresses, temperature and environment in which they are required to perform. The design life is typically in excess of 100,000 hours which is ten times longer than for aircraft engines from which much of the necessary technology was derived. This difference and the much larger sizing of power generating turbine components prompts significant divergence from aircraft engineering practice in many instances. Also for the land based turbine considerations of weight are considerably less crucial.

Service conditions and consequent materials requirements vary primarily in relation to their position in the gas turbine. For convenience it is customary to discuss them in three distinct areas viz.: a) The compressor; b) The combustion section and c) The turbine. This methodology will be pursued here.

2.0 *CURRENT MATERIALS SELECTION CRITERIA*

2.1 *Compressor Materials*

Compressors in large industrial gas turbines are required to pass over 400 kg/sec of ambient air and raise its pressure by a factor of 14/1/. The air is supplied primarily to facilitate fuel combustion but because of current material limitations in the high temperature sections of the turbine up to 25% of the air is utilized for component cooling. Maximum service temperatures in the compressor section rarely exceed 400°C. Centrifugal and bending forces are high and depending upon the local air quality some potential for corrosion may exist/2/. Other reported problems concern incidence of both wear and fretting fatigue at compressor blade to disc attachment interfaces. Preventative measures include the introduction of compressive stresses into disc roots by shot peening and the application of resistant coatings such as Cu-Ni-In overlaid with molybdenum disulphide/3/. Compressor efficiency is critically dependent upon maintenance of very smooth airfoil surfaces and minimal clearance between blade tips and casing components.

Considering the foregoing, the moderate temperature strength and relatively mild corrosion resistance requirements of compressor blades are usually met with martensitic stainless steels of either the 12 wt% Cr A.I.S.I. type 403 variety or the somewhat heavier duty 17 wt% Cr precipitation hardening 17-4PH type/1/. Prolonged service in the temperature range from 370 to 480°C severely embrittles the latter material and therefore limits its application to cooler parts of the compressor/4/. For some moderately severe corrosion conditions it may be necessary to specify nickel based austenitic alloys for the higher temperature compressor components/5/. Compressor stationary guide vanes employ the same materials as the rotor airfoils. For both, fabrication methods have encompassed precision forging, machining and precision casting. The excellent weldability of vane and airfoil materials has facilitated repair of both impact and minor corrosion damage/5/. Coating for corrosion protection is only rarely necessary (eg. in salt laden marine environments) and in such cases either nickel-cadmium plating or aluminum-rich sacrificial formulations have provided significant protection.

Compressor discs and rotors operate at temperatures considerably below those of the vanes and airfoils. Resistance to fatigue and brittle fracture mainly dictate materials selection criteria. Discs are invariably forged and for components with section thickness below 100 mm, quenched and tempered low alloy steels such as A.I.S.I. type 4340 have performed adequately/5/. Heavier sections require air hardening steels such as A.I.S.I. type 422. Most machines have utilised discs shrunk onto rotor shafts. Alternative designs have dispensed with shafts and used stacked discs which are either welded or bolted together. Improved fatigue resistance accompanies reduction in size and concentration of non-metallic inclusions. Refining methods for disc materials therefore often include either vacuum arc or preferably electro-slag remelting/6/.

Casing materials for compressors are typically either gray iron or carbon steel castings to A.S.T.M. specifications A278 or A356 grade 1 respectively. When fabricated by welding of carbon steel plate, a commonly specified choice is A.S.T.M. A515 grade 70. An abradable coating of aluminum applied to selected areas of the casing wall effectively improves compressor efficiency by minimizing the gaps between the airfoils and the casing/5/.

Tables 1 and 2 summarize respectively the compositional and mechanical property requirements for gas turbine compressor materials. Major changes in these are neither required nor expected in the near future.

2.2 *Combustion Zone Materials*

This zone consists essentially of fuel nozzles, combustion chambers where the fuel is burned, and transition ducts to carry the high temperature gaseous products of combustion to the power turbine. Combustion chambers and ducts are welded sheet metal fabrications. Materials of construction must have good formability and weldability. Service conditions combine high temperature operation with exposure to an atmosphere which may alternate between oxidizing and reducing. Depending on the fuel used, various deleterious impurities may also be present. Chlorides, sulphur compounds and alkali metal salts are particularly detrimental. Combustion section materials are required to resist oxidation, general corrosion, creep, low and high cycle fatigue and thermal shock over a range of temperatures from 20 to 870°C. Air cooling is necessary for temperature control. A number of design innovations have attempted to provide optimal distribution of the cooling air flow/7/.

For oxidation and general corrosion resistance combustion section alloys have approximately 20 wt% of chromium. Traces of rare earth elements are often added for additional protection. High temperature strength is assured by incorporating a fine dispersion of very stable precipitates to retard both dislocation movement

and grain boundary migration. The precipitates must resist both dissolution and growth for prolonged periods when subjected to stress at high temperature. Useful precipitates include refractory metal carbides, gamma prime (ie. Ni_3Al or Ni_3Ti) and rare earth oxides. The latter are incorporated into a suitable matrix by the relatively modern mechanical alloying process. When present in a creep resisting austenitic nickel based matrix such dispersions are very effective.

Tables 3 and 4 provide relevant details of current combustor material optimisation for each of the three aforementioned microstructural dispersion strengthening types. A particular advantage for Nimonic alloy 263 is its slow precipitation hardening response which helps in the avoidance of repair weld cracking problems and facilitates use of a simple ageing procedure for post-weld restoration of heat affected zone properties. Conversely, oxide dispersion hardened alloys are particularly difficult to weld successfully. Electron beam and laser welding have provided only modest results. Full realization of the potential of these alloys will probably depend upon development of suitable brazed or mechanical joints.

The best available alloys are operating at temperatures close to their melting points. Near term developments will therefore concentrate on improved designs, particularly in cooling systems and thermal barrier coatings/10/.

Included in Tables 3 and 4 are particulars of combustor fuel nozzle materials. When compared with the sheet metal components, operating conditions are comparatively far less arduous and satisfactory performance generally results from selection of cast A.I.S.I. type 309 or 310 stainless steels. For greater longevity a brazed assembly of Hastelloy X alloy castings and Inconel alloy 718 wrought components has been used/8/.

Finally, the normal operating temperatures and thermal cycling experienced by combustor casing materials demands consideration of tough, low cycle fatigue defect tolerant low alloy chromium-molybdenum steel castings. Details of suitable formulations appear in Tables 3 and 4.

2.3 *Materials for the Power Turbine*

Operating conditions combine the high centrifugal loading and high cycle fatigue of the compressor section with the elevated temperature, low cycle thermal fatigue and potentially damaging atmosphere of the combustion zone. Again maximum alloy temperatures are controlled by air cooling and currently do not exceed 870°C. Blades and vanes may be either forged or cast; discs are invariably forged. Blade castings are sophisticated; they are often hot isostatically pressed to seal internal porosity and the casting technique may be refined to provide either directional solidification or a single crystal casting. These techniques provide substantially improved creep properties by either minimizing or eliminating the areas of creep susceptible grain boundary material which are in the planes of tensional stress at the very high normal operating temperatures. Some experimental work on rapid solidification technology was also undertaken. Preliminary results were disappointing. Directional solidification and single crystal technologies are well established for routine production of aircraft engine turbine blades. Some development will be required to scale up the processes to manufacture the much larger blades required for utility turbines. Tables 5 and 6 contain appropriate information on blade materials in current turbine designs.

Power turbine vanes in large land based units may utilise the same nickel based superalloys as the airfoils. However, foundry difficulties are such that only single vane segments have been cast. Cobalt alloys have been successfully cast into multi-segment vanes. Their resistance to creep, oxidation and low cycle fatigue is generally satisfactory; this together with the foregoing makes them

strengthened by the refractory elements tungsten and tantalum and by fine precipitates of both chromium and zirconium carbides. Chromium also enhances resistance to both oxidation and general corrosion. First stage vanes require a high degree of air cooling. The necessary cooling passages are often incorporated by the welding or brazing of inserts. The vane material selection must be compatible with this approach. Occasionally the brazing and solution heat treatment cycles are one and the same. Final alloy properties are then achieved by a suitable ageing heat treatment. Periodic weld repairs are necessary to ensure an economic life expectancy. Pre-weld heat treatment is usually necessary to provide a more readily weldable metallurgical condition. Welding consumables are of similar composition to that of the base material. The gas-tungsten arc process is normally used but electron beam and plasma techniques have been successfully applied. Development of easier fabrication for oxide dispersion strengthened alloys would offer advantages for stationary vane production. Currently emphasis is directed toward designs for more efficient cooling and use of advanced thermal barrier coatings. Tables 5 and 6 include relevant details on the more recently developed stationary vane alloys.

3.0 *GENERAL REQUIREMENTS OF COATINGS FOR COMBUSTION TURBINES*

Coating the blades and selected components of the turbine section has become a well accepted means of high temperature protection for utility combustion turbines. This activity has been particularly intensive during the past decade as the possible operating limits are stretched by improved high temperature mechanical properties of new superalloys. In order to take advantage of the higher efficiencies possible through these new materials, coatings must be used to protect blades and vanes. These coatings must offer protection against effects such as hot corrosion and high temperature oxidation while allowing for a reasonable operating period before maintenance. Many of the higher strength alloy systems being developed for blades have experienced improved high temperature mechanical properties at the expense of reduced high temperature corrosion resistance. Corrosion resistance requirements will become even more arduous as the fuels used in utility turbines become lower quality due to financial incentives and supply limitations. The expectation to use fuels of various compositions over the expected life of the turbine will place further pressure on turbine components to be corrosion resistant in a variety of environments.

Utility turbine blades can be expected to encounter gases at about 1 MPa, 1150-1200°C and a velocity of 300 m/s. With internal blade cooling, the maximum coating temperature will likely be in the range of 850-900°C. This may increase in the future with the higher gas inlet temperatures (up to 1350°C) of advanced turbines or reduced blade cooling gas. The blade coatings are also subjected to cyclic and constant operating stresses as a result of thermal cycling and turbine rotation (up to 16 MPa at 150 to 2000 Hz). The gases encountering the coating are oxidizing as turbines are typically operated with an excess of air. Depending on the fuel composition, various potentially harmful constituents can be deposited on the coating and these include SO_2, SO_3, SO_4, O_2, CaO, MgO, K_2O, NaCl, HCl and V. In order to combat these chemical effects, a wide variety of coatings have been investigated which include multicomponent alloys and metals in combination with ceramics.

Based on these described conditions, a turbine coating is exposed to a myriad of potential failure modes. These include:

i) high temperature oxidation (spalling)
ii) low and high temperature hot corrosion
iii) cyclic temperature corrosion by chlorides and vanadium
iv) high temperature creep

v) thermal fatigue
vi) high temperature erosion
vii) interdiffusion degradation
viii) coalescent Kirkendall void formation
ix) propagation of as-applied coating flaws

The components of the turbine section are typically coated with a diffusion or overlay coating whose primary function is oxidation/corrosion protection. Higher temperature operation is possible by using thermal barrier overlay coatings which are typically based on a mixed oxide composition.

The combustion section of turbines has similar coating requirements to the turbine section. The coatings are usually applied on nickel based alloys for oxidation resistance and to act as thermal barriers. Since maintaining exact blade geometries is not a requirement in this section, the requirements for the coating can be considered less stringent.

The compressor section operates at significantly lower temperatures (<400°C) and coatings are primarily aimed at reducing wear and erosion, although corrosion protection is still an issue. The types of coatings used include oxide based coatings to protect exposed sections and metallic based coatings to protect wear prone areas, such as the roots of blades.

Since the most serious problems and stringent requirements for coatings exist in the turbine section, the discussion covering coatings will be focused on those requirements.

4.0 *METHODS OF APPLYING METALLIC AND CERAMIC COATINGS*

The technology of applying coatings has advanced significantly and finds use in all facets of technology from fastener protection to computer chip manufacturing. Virtually all the various types of coating technologies can be used for combustion turbines although there are advantages and disadvantages depending on the coating system chosen. In order to provide a complete, systematic evaluation of coatings for combustion turbines, each type of coating method has been reviewed with a view to establishing its effectiveness and the potential for implementation of research and development efforts. The more important methods are described in this report.

The various coating methods can be divided into various categories based on the general type of deposition mechanism responsible for application of the coating. This categorization is summarized in Table 7 which indicates six general mechanism categories and three application methods which do not strictly fall into one of the six general categories.

4.1 *Physical Vapour Deposition*

Physical vapour deposition (PVD) techniques can be used to deposit metals, alloys, intermetallics and refractory compounds. The three PVD processes are vacuum evaporation, sputter deposition and ion plating. The unique attribute of PVD is that the coating results from non-equilibrium processes so that any coating can be deposited onto virtually any substrate/22/. Originally PVD was used to deposit single materials and thus no chemical reactions were necessary. At present, compounds are usually deposited by PVD utilizing a gas phase reaction which is similar to chemical vapour deposition processes. Deposition rates vary from 10^{-3} to 25 μm per minute with the higher deposition rates only possible with high energy electron beam evaporation of the coating source.

From a historical perspective vacuum evaporation did not progress with respect to industrial applications until the development of industrial vacuum apparatus

in the late 1940's. Sputter deposition and ion plating were initially developed in the early 1960's primarily as thin film technology. At present all these PVD processes are used to prepare not only thick films but bulk deposits of materials which are difficult to process by more traditional means.

The various PVD deposition techniques follow a basic three step process which can be described as follows:

1) Forming the material to be deposited by changing states from condensed to vapour and where compounds are to be deposited, a gaseous reaction step.

2) Transporting the vapour from the source to the substrate.

3) Condensing the vapour, followed by film nucleation and growth.

This deposition route has some distinct advantages for turbine component coating applications. All types of materials can be deposited and since the source of the coating is removed from the substrate, the substrate temperature can be independently controlled. The coating characteristics are good since the vacuum allows high purity to be achieved, as-deposited surface finishes are equivalent to the substrate and reasonable bonding can be achieved.

PVD coatings are usually very distinct overlay coatings with a well defined separation between the coating and substrate. This is in contrast to diffusion and ion implanted coatings which have a significant transition region between the coating and substrate.

4.1.1 *Sputter Deposition*

In the sputtering process as shown in Figure 1, a glow discharge is used to remove atoms from the cathode source which then deposit on the substrate. Typically only 1% of the bombarding energy yields sputtered or ejected atoms with the majority of energy causing the cathode to increase in temperature. Sputter deposition techniques are typically low rate and low yield which is not suitable for most combustion turbine applications. In order to increase the deposition rate, modifications to single source sputtering such as triode sputtering, magnetron sputtering, RF sputtering and combined sputter ion plating have been tried.

Sputter deposition of Al_2O_3 is possible using reactive sputtering but the reactive gas tends to poison the cathode surface resulting in extremely low coating efficiencies. CoCrAlY has been deposited by sputtering but the coatings were either cracked or had a poor microstructure/23/.

Sputter deposition does not appear to be a suitable method for coating turbine parts at this time. The major drawbacks appear to be the sophisticated nature of the processing equipment, the low deposition rate, difficulty in obtaining a relatively defect free coating and lack of technical data.

4.1.2 *Vacuum Evaporation*

Vacuum evaporation deposition is most effective using an electron beam as the heating source as shown in Figure 2/12/. Evaporation techniques can be used to deposit pure metals, alloys, intermetallics, refractories and mixtures of these. When a multi-element coating is required, the problem of differing vapour pressures must be addressed in order to control the vapour phase composition and in turn the resulting coating composition. This can be accomplished by either multiple, controlled sources or a single rod of a composition to give the correct vapour pressures. The single rod fed, electron beam source technique requires the simplest control requirements and has been used to deposit a complex NiCrAlY

coating. Table 8 provides a brief description of various evaporation processes/25/.

There are many equipment variations to the basic electron beam evaporation technique. The vapour source can be heated by resistance, induction, ion beams, arcs and lasers. As indicated in Table 2, the deposit can be altered by using a plasma and an electrically biased substrate. The coating material can also be fed to the evaporator as a powder.

Oxides such as Al_2O_3 can be deposited but on vapour formation by electron beam heating, the compound is fragmented into various components. The final stoichiometry of the coating will depend on the deposition rate, ratios of fragments in the vapour state, surface mobility of fragments, reaction rate of fragments on the substrate and impurities on the substrate. It has been found experimentally that Al_2O_3 is deposited with an oxygen deficiency which can be corrected by introducing a low oxygen partial pressure into the substrate environment/24/.

The high deposition rates of electron beam evaporation units has made this the PVD method of choice for coating aero turbine blades. Continuous coating of blades has been accomplished with CoCrAlY, CoCrAlYTa and NiCrAlYSi in the late 1970's and was found to give better coatings than those possible with plasma spraying at that time. It has been reported that this technique has been used to coat millions of aero turbine blades which can justify the high capital cost of an evaporation unit/25/. This technique is recognized as being difficult to carry on due to having to maintain a well characterized molten pool/26/, manipulate blades inside the vacuum and form consistent coatings with MCrAlY compositions. To avoid some of these problems, developmental work with ion and sputter ion plating is being carried out.

4.1.3 *Ion Plating*

The ion plating technique is similar to the evaporation process except that a glow discharge is used to ionize some of the vapour atoms as shown in Figure 3. The substrate is the cathode and some mixing of the substrate and vapour takes place due to the energy of incident vapour atoms. More consistent coatings are possible with this technique than with simple evaporation since the gas is scattered and entrainment and re-deposition of ions takes place on the charged substrate.

4.2 *Chemical Vapour Deposition*

Chemical vapour deposition (CVD) is a process whereby a thin coating is developed on a substrate using a chemical reaction between the gas phase and solid substrate. Depending on the material deposited, the temperature of the reaction to produce the coating can be anywhere from 200 to 2200°C although most turbine CVD coatings, including those which are silicon based, are formed at about 1,000°C. In addition to temperature effects, a CVD coating procedure must also consider the potential deleterious effects of corrosive attack by the reaction gas or reaction by-products.

The CVD process can take several forms based on how the deposition reaction takes place. In one technique, metal-carbonyl gaseous compounds which are stable at low temperatures can be passed over a heated substrate causing the metal to be deposited as a result of compound breakdown. Other gaseous methods include hydrogen reduction with metal deposition and more complex reduction reactions which are used to deposit carbides, nitrides and oxides. These types of coatings typically involve the growth of a distinct layer whereas for turbine blade applications, elements diffuse into the substrate and form a coating exhibiting a concentration gradient. A combination of these two types of coatings occurs

when both deposition of the coating material and a diffusion reaction is used to form a complex coating. The usual CVD method used to coat turbine parts is pack cementation with the diffusing species source being a solid.

The various CVD techniques have been developed extensively on a commercial basis for all requirements including high temperature turbine protection. Since this technology is particularly industrial-application based, the open literature usually does not describe details of the various proprietary techniques. As a result of the extensive industrial activity in CVD development, the following CVD techniques can be listed:

1. conventional CVD
2. plasma or laser assisted CVD
3. pack and slurry techniques.

Some of the general advantages offered by CVD techniques include:

1. not a line-of-sight method
2. relatively simple equipment
3. good composition control
4. coatings are dense and relatively defect free

4.2.1 ***Pack Cementation***

The most commonly used diffusion coating process to protect hot section turbine parts has been the pack cementation CVD process. This technique can be used to deposit aluminum, chromium and silicon (ie aluminizing, chromizing and siliconizing) rich layers on superalloys. Although many of the other coating techniques such as plasma spraying and physical vapour deposition can be used to deposit controlled composition coatings, the long history of industrial use of pack cementation often makes it a supplier preferred technique. In addition to familiarity with the process, industrial users are also attracted by its low overall cost as compared to other techniques.

The pack cementation process in its simplest form involves imbedding the component to be coated in a powder mixture held in a furnace. There has been some effort to separate the pack from the component since pack particles can sometimes be incorporated into the coating during its growth. The most commonly used aluminizing pack cementation method has the substrate imbedded in a powder pack of aluminum powder (typically about 15 weight percent), halide activator and inert diluent/16/. The inert diluent prevents the pack material from sintering together since typical pack cementation temperatures range from 700 to 1100°C. In addition to aluminizing, chromizing and siliconizing are commonly performed although this method has also been used to deposit titanium and zirconium based high temperature coatings on superalloys.

The overall operating sequence for pack cementation (aluminizing) is given in Figure 4 for a nickel based superalloy/15,17/. The source of aluminum can be either pure aluminum or some alloy, typically with chromium, as the necessary aluminum activity of the pack is established by the aluminum concentration of the solid source. The aluminide layer forms over several hours and results in a variety of aluminides which can be identified in the phase diagram of Figure 5/18/. Typically the outer regions of the coating has more aluminum and sometimes results in the formation of δ-phase (Ni_2Al_3) which is an undesirable intermetallic, being brittle and having a low melting temperature. Diffusion treatments can be used following pack cementation in order to dissolve any δ-phase which is formed.

The aluminizing coating process of a nickel superalloy as given in Figure 4, shows the halide activator (NH_4Cl) forming gaseous aluminum halides ($AlCl_3$). The

aluminum mass transport from the pack to the substrate is a combination of diffusion and convection. At the substrate surface the aluminum halide reacts due to the high temperature and forms an aluminide with subsequent diffusion into the substrate. The formation of the various aluminides can be explained by considering the solid state diffusion rates of the Ni-Al system and the rate of aluminum arriving at the substrate. A low activity of aluminum results in a ß-phase (NiAl) which is formed primarily by nickel diffusion out into the coating. A high activity of aluminum results in δ-phase which is formed primarily by aluminum diffusing into the substrate. Under conditions of the coating growing outwards from the substrate (ie, low aluminum activity), particles from the pack can become incorporated into the coating.

The incentives to use pack cementation to coat turbine blades and other parts arise from this technique's inherent ability to coat geometrically complex parts, form high melting point deposits and form coatings with a relatively simple procedure. There are however, some significant drawbacks to the pack cementation method which can be overcome by techniques such as plasma spraying. One disadvantage of pack cementation techniques is that the entire component must be heated to a high temperature which can be cumbersome for larger components. Also, since this is a diffusion process with a typical diffusion profile, the composition of regions beneath the desired coating are affected which is detrimental to the physical properties. These detrimental effects depend on the exact interaction between the substrate and diffusing species. Possible results include porosity, brittle structures, cracks, low corrosion resistant structures and low melting temperature phases.

Pack cementation with aluminum was initially used on aero turbines in the United States beginning in the 1950's for first stage vanes. In the 1970's aluminizing following a chromizing step was used on land based turbines. The development of aluminizing treatments was primarily motivated as a technique to provide hot corrosion resistance. Apart from an initial chromizing treatment, the only significant development in this process has been the addition of chromium or platinum to the aluminum coating which provides added protection when high levels of sulphates are present.

4.3 *Plasma Sprayed Coatings*

Plasma guns were developed in the 1950's to melt ceramics and metals. During the 1960's and 1970's this technology was adapted to spray metallic and ceramic coatings on substrates to enhance the base material's properties. At present, plasma spraying technology has become a sophisticated process which is widely used for extreme service industrial applications and aircraft engines/12/. The benefits of plasma spraying compared with other coating techniques include high deposition rates, minimal disturbance of the base material properties, ability to melt a wide variety of materials and ease of application for operators.

A typical plasma gum consists of a bullet shaped cathode within a cylindrical anode. A technique is used to apply a voltage at a fairly high current across the electrodes and an arc is initiated which ionizes the argon gas flowing between the electrodes. Molecules are dissociated and neutral atoms are ionized by the initial high energy ions until the flowing gas becomes a plasma. As a result of the gas flow and shape of the electrodes, the plasma typically appears as a plasma flame coming out of the anode nozzle. The power consumption level for hand held plasma guns ranges from 10 to 80 kW although industrial plasma melting torches can consume power in the several megawatt range.

The most commonly used plasma sprayers are small hand held units although there are many systems which are automated. A complete plasma spraying facility is made up of the following components:

- Plasma torch
- Power supply and control
- Gas control
- Particle feed system
- Cooling water
- Protection, safety and auxiliary systems

The power supplies used with plasma torches are usually DC with minimal ripple. A typical DC rectifier system will output voltage with a 3 to 6 percent ripple content. If the voltage ripple is excessive, an unstable arc can be developed. To maintain the ripple free voltage requirements, the power supplies usually operate in the drooping voltage-current regime. This voltage-current relation damps out any fluctuation rather than allowing fluctuations to become large and unstable. Ammeters and voltmeters are used to monitor the power.

Powder supply systems are based on various techniques such as aspirators and fluidized beds which get the particles into the gas stream. The supply system must be capable of supplying a well controlled amount of powder which is well distributed in the gas. Properties of the particles themselves are important in order to get the correct feed to the plasma area. Typical powders are approximately spherical in shape with diameters ranging from 0.1 mm to 0.005 mm. For a particular application a narrow size range gives the best results since melting and particle acceleration are more consistent. An optimum particle size is always possible since particles too small can vaporize, oxidize excessively, block torches and loose momentum once having exited from the plasma. Conversely, too large particles do not melt sufficiently, are more difficul. to accelerate and result in less dense deposits.

The dense plasma in a plasma gun contains most of its energy in the form of enthalpy which results from the numerous high energy particle collisions. Gas temperatures at the nozzle of a plasma gun can range from 10,000 to 15,000°C/21/. The heat content per unit mass of the plasma flame can be increased by using gases with higher enthalpies (eg, adding H_2 to Ar). A plasma jet can reach supersonic velocities and extremely high temperatures as a result of the electric and accompanying magnetic fields generated by the plasma gun's geometry.

In order to deposit a material with the plasma gun, a secondary gas stream with the entrained coating material is injected into the high velocity plasma. The high temperature of the plasma and heat from reactions in the plasma melt the particles and accelerate the particles outward. Particle injection is preferred before the anode so that a long plasma residence time for the powder can be achieved. A powder injection problem which is sometimes encountered using this powder feed method is particles coating the anode which can lead to overheating and blockage. This can be avoided by injecting the powder downstream of the anode which reduces the plasma gun's efficiency. Typical particle upper velocities are 120-350 ms^{-1} although values as high as 550 ms^{-1} can be achieved which substantially exceeds the 331 ms^{-1} speed of sound in air/11/.

It is critical that several factors are carefully controlled in order to obtain a suitable deposit. The heat imparted to the particles must be sufficient to melt yet not vaporize the particles. This is accomplished by judiciously controlling particle composition, particle size, particle injection point, particle speed, injection gas composition, plasma heat content, plasma velocity and plasma composition. Controlling these variables which in turn establish the exiting particles' characteristics from a plasma gun is primarily based on experience combined with trial and error. There have been some studies conducted to establish a fundamental understanding of plasma gun operation although the subject is still far from being well understood.

Experimental work evaluating the temperature reached by particles in a plasma gun are primarily aimed at quantifying the effects of time in the plasma, catalytic surface activity, emissivity, heat capacity, thermal conductivity and shape/13/.

Plasma spraying of turbine components began in the mid 1970's and the early results were not very good. As more experience was gained, the quality of coatings has improved to the point that plasma sprayed coatings are among the best.

4.3.1 *Plasma Spray Coating Characteristics*

A plasma sprayed coating develops its adherence as a result of both chemical and mechanical bonding. The best adherence characteristics are achieved with a roughened substrate achieved by mechanical abrasion. The irregularities of a roughened surface provide key-ways into which molten droplets can penetrate, solidify and be locked in. Following completion of the first layer, the deposited "splats" provide further surface irregularities for subsequent deposits to adhere to. Since the particles are molten, some fusing between the particles and substrate takes place to form chemical bonds as well as interdiffusion assisted bonding.

When molten particles hit the substrate, the cooling rate is extremely high which results in a very fine grain size. There are numerous flaws in the structure, particularly if the spraying is done in air which leads to oxidation and solidification before striking the surface of the substrate. The high rate of particle cooling and controlled coating application rate allows a surface to be coated without a significant increase in its temperature which would take place with techniques such as weld overlaying. Flaws in the coating must be controlled to ensure mechanical strength and suitability as a corrosion barrier. Some flaws, such as pores improve insulating properties in applications such as thermal barriers and are in fact beneficial. This demonstrates that if close control of the spraying process was possible, coatings could be optimized for the characteristics necessary for the particular application. In the case of more brittle coatings such as ceramics, pores can be used to produce a tougher material as the pores act to arrest crack propagation. Coatings exhibiting good toughness are particularly desirable during temperature changes since large stresses can be developed due to different thermal expansion coefficients. Metallic bond coatings are typically used to alleviate thermal strains in multicomponent coating systems where a ceramic thermal barrier coating is used.

When coatings exhibiting fewer defects are necessary, plasma spraying can be carried out in an inert atmosphere or a partial vacuum. Applying a coating in a partial vacuum dramatically reduces the levels of voids and oxide particles. One additional benefit of working in a vacuum is that droplet velocities are higher so particles deposited have a lower as-deposited profile resulting in dense coatings. Vacuum spraying is typically useful for metals and absolutely necessary when more reactive metals such as zirconium are part of the deposit. The oxidation/corrosion resistant metallic or bond coatings used on turbine blades are normally sprayed in a partial vacuum.

4.3.2 *Plasma Spraying Operating Considerations*

When using a normal plasma torch, the operator can influence variables, not related to initial equipment set-up which will affect the quality of the coating. These variables include the incidence angle of the spray stream, the torch to substrate distance and the rate of travel across the substrate. It has been found that a spray stream perpendicular to the substrate surface results in the most adherent and dense coating. Many of the operating variable problems can be overcome by using automated techniques ranging from using lathes to computer controlled movement of parts. Automated plasma spraying is most amenable to

simple parts which require simple automation or where large numbers of identical parts can justify the set-up cost for a complex automated coating procedure.

4.3.3 *Substrate Requirements for Coatings*

In order to obtain an adherent coating, the substrate must be as clean as possible and have its surface roughened for mechanical bonding. Cleaning the surface depends on whether the substrate can be installed in a chamber. If a chamber is available, techniques such as sputtering can be used to clean the surface. The most commonly used method is grit blasting which results in fairly sharp surface features which promote mechanical bonding. Again, processing in an inert, controlled environment can improve the level of cleanliness of the substrate.

Areas of the substrate not to be coated are typically masked before spraying rather than grinding after spraying. Masking depends on the state of particles hitting the substrate so tapes, paints and metallic foils are used.

5.0 *ROLE OF PROTECTIVE COATINGS IN COMBUSTION TURBINES*

The general reasons for applying coatings to blades (and other high temperature components) in combustion turbines can be stated as the following:

> *"To maintain the turbine blades' shape for as long as possible which maintains the machine efficiency (optimum blade/gas load dynamics) and to prevent catastrophic disintegration failure".*

The need for coatings has developed as base materials were modified to improve high temperature strength at the expense of high temperature corrosion/erosion resistance. The primary metallurgical technique of doing this with nickel based alloys was to reduce chromium levels while increasing aluminum (and to some extent titanium) which increases the number of strengthening γ' particles. This reduction of chromium significantly reduces the protective chromium oxide scale making the superalloy more prone to hot corrosion. Adding tungsten and molybdenum as solid solution strengthening additives has been found to reduce hot corrosion resistance. The complex polycrystalline nature of the advanced superalloys operating at high temperature also presents the opportunity for creep rupture and low cycle thermal fatigue cracking initiated at grain boundaries. Low cycle thermal fatigue can be enhanced by the presence of chloride ions which requires attention to the type of fuel being used/9/.

Although the cobalt based alloys demonstrate superior resistance to hot corrosion and oxidation, coatings are still necessary to obtain reasonable life at high efficiency turbine operation. The same can be said for the oxide strengthened and single crystal blade technologies which are currently under development.

A coating or coatings applied to a turbine blade will not completely stop the deterioration of a blade. The coating instead adds life by slowing down the relevant degradation mechanism taking place to meet the design life requirements. This ability of the coating to perform its purpose is a complex function of various material properties including hardness, oxidation kinetics, diffusion rates and gas permeability. It must also be recognized that a coating can only be justified if economic benefits exceeding its cost can be obtained. These economic benefits can take the form of reduced maintenance, longer life and expanded fuel options. The use of less expensive fuel may be possible as the coating will resist the typically more corrosive and erosive gas load associated with the "dirtier", less expensive fuel grades.

In order for a coating to be considered for use, it must demonstrate some specific functional, operational, maintenance and economic requirements which can be listed as follows (order of importance is dependent on the particular application and environment):

- Resist oxygen hot corrosion (oxidation)
- Resist sulphate hot corrosion (for low Cr superalloys) of both Type 1 (800-1100°C, high turbine power level) and Type 2 (700-750°C, low turbine power level)
- Improve or not degrade high temperature creep properties.
- Improve or not degrade high temperature fatigue properties.
- Provide erosion protection
- Be compatible with substrate and not affect operational requirements.
- Must adhere to substrate.
- Demonstrate uniform and consistent properties.
- Be cost effective.

These requirements indicate that any evaluation of a coating must ultimately take the form of a coating/substrate system evaluation for a particular set of operating conditions.

5.1.1 *Coating Effects on Creep*

Creep is a more significant problem for blades on a turbine operating as a base load unit at near continuous operation since fatigue failures are usually not an issue. The creep resistance of blades is highly dependent on the thermal history of the blade as this can have detrimental effects on the microstructure. As an example, diffusion coating heat treatments of Udimet 520 were found to increase the density of grain boundary carbides which reduced the creep strength/20/. The loss of creep properties as a result of heat treatment is dependent on the particular coating-substrate system. It was found that the heat treatment used to bond a CVD silicon coating on IN-738 LC causes a reduction in creep strength whereas the same coating procedure has no effect on Nimonic 105/14/. It is also possible to coat and heat treat IN-738 LC with a plasma sprayed NiCrSi coating without any significant effect on the system creep strength/31/. The primary reason for creep strength reduction is the growth of grain boundary carbides in susceptible alloys. The growth of carbides can be stimulated by the coating application heat treatment as well as diffusion of elements from the coating into the substrate.

5.1.2 *Coating Effects on Fatigue*

Low cycle thermal fatigue is particularly a problem for turbine units used for peak power service which requires frequent start/stop cycles. Any coating used must be able to withstand thermally initiated mechanical stresses developed at the surface and coating to substrate interface as temperatures change. If the coating does crack, the most serious problem would be extension of the crack into the substrate. Materials such as directionally solidified and single crystal alloys could lose much of their appeal if fatigue resistant coatings are not used. These advanced processed metals have superior mechanical properties since grain boundaries are not a factor in initiating fatigue cracks. Incorrectly applied coatings could deteriorate their inherent ability to resist fatigue cracking by acting as a crack initiating mechanism. This same mechanism could apply to polycrystalline blade materials.

Some coating materials have been found to resist fatigue cracking better than others. MCrAlY coatings for instance, are believed to be superior to diffused

aluminide coatings in resisting low cycle thermal fatigue/10/. This finding is likely primarily a result of MCrAlY coatings having thermal expansion coefficients closer to those of the superalloy blades as compared to diffused aluminide.

A potentially less serious problem of fatigue cracks in coatings, but nonetheless undesirable is that they expose the substrate. This can lead to corrosion, possibly accelerated, of the substrate.

As a result of rapid cooling, plasma coatings typically have residual stresses which result in the coating being in a state of tension. These residual stresses must be added to any cyclic stresses which exist as a result of operating conditions. In areas of the turbine where components are designed and fabricated to withstand extreme fatigue conditions, coatings can have a deleterious effect since the fatigue life of the coating will usually be exceeded before the substrate.

5.1.3 ***Coating Effects on Corrosion***

It can be expected that the most important potential failure mechanism to be encountered will be some form of oxidation or sulphidation as a result of oxygen and sulphur from the fuel and air. The prevalent aluminum coatings of the past on their own do not provide the necessary protection from sulphidation as sodium sulphate can react with aluminum oxide to form sodium aluminate which provides no protection to the substrate/14/. Improvements can be made to aluminum based coatings through the addition of platinum although superior sulphate hot corrosion resistance is possible with coatings such as CoCrAlY (35% Cr with 2-10% Si) and MCrSi(Co or Ni based).

The corrosion performance of a specific coating will be highly dependent on the particular gas composition in the turbine. The resistance of a coating to any form of corrosion is dependent on its composition which must not change with time. At the high operating temperatures encountered, diffusion can take place in a specific coating/substrate system such that the protective properties are lost by diffusion of elements either from the coating into the substrate or from the substrate into the coating. In some cases, this interdiffusion can be minimized by using interlocking phenomena as the mechanism which primarily accounts for adhesion. However, without significant atomic bonding between the coating and substrate, any stress present would tend to cause cracking and chipping with subsequent corrosion. In the case of a coating system made up of various layers, appropriate adhesion must exist at each coating interface.

If high temperature operation requires the use of ceramic coatings, careful selection must be made in order to extend the component life if corrosives are present. Normally an yttria stabilized zirconia would provide the best thermal barrier but it potentially suffers from liquid sulphate attack and in this case, other ceramics must be considered. Zirconia coatings can fail due to hot sulphate corrosion either by freezing/thawing of sulphates or acidic dissolution of Y_2O_3 stabilizers/29,30/.

5.1.4 ***Coating Effects on Wear Resistance***

There are three major types of wear mechanisms which can take place during turbine operation and they are:

Adhesive Wear: Often described as galling, scuffing or seizing and takes place at sliding contacts where no separating layer acts as a lubricant.

Abrasive Wear: Usually caused by hard particles striking a surface leading to cutting impacting and ploughing or erosion of the substrate.

Fretting Wear: Results from low amplitude loads and/or motion causing erosion of the substrate.

In addition to these major types of wear, corrosion can be added as a contributing mechanism which augments the deleterious effects of wear.

The best erosion resistance would be expected from ductile coatings which would absorb energy from impacting particles by deforming rather than chipping off. If the coating can be locally removed, thereby exposing the blade material, accelerated corrosion of the substrate can also take place. The severity of erosion will be dependent on the composition of the burning gases and any filters used.

5.1.5 *Coating Effects on Functional Requirements*

Any component which is coated must maintain its designed functional requirements. One of the main influences in meeting this criteria is the smoothness of the coating which must be adequate so that it does not to disrupt gas flows and reduce efficiency. This usually means that the coating must have a surface roughness equivalent to a machined or precision cast blade. The coating must also maintain its composition to retain the desired properties which necessitates low levels of interdiffusion. Excessive interdiffusion can result in undesirable phases or loss of properties by the substrate. Good adhesion of the coating must exist in order for the coating to maintain its protective properties and prevent secondary damage to the turbine by spalled pieces. In order to achieve this, factors to be considered are surface atom bonding energies, surface roughness and diffusion activation energies. Although all of these factors contribute to coating adhesion properties, depending on the specific coating/substrate system the relative importance between these three influences can change.

The effects of coatings on the strength of blades can be deleterious if not properly applied. This is particularly true of ceramic coatings which are notch sensitive and have poor impact strength and if allowed to influence the substrate, can lead to failure. It has been reported that many coatings such as Al, SiAl, PtCrAl and NiCoCrAlY have virtually no effects on the strength of IN-738 and IN-738 LC/16/.

5.2 *Coating Development*

Many coating systems have been developed for turbines and optimized for protection against oxidation, hot corrosion and erosion as well as acting as a thermal barriers. Oxidation resistant coatings on substrates such as IN-100, IN-738 LC, IN-792 and Rene 80 have included Al, NiAl, CoAl, NiCrSi, $CrSi_2$, AlCr and aluminides. Where the combination of oxidation and hot corrosion resistance is necessary, coating systems have tended towards MCrAlY, Cr-Al, Si-Al, Pt-Cr-Al and Al. When hot corrosion resistance is the major objective, the types of coatings used are Si base, CrNi, MCrAlY and Pt-Al. Thermal barrier coatings are typically based on either ZrO_2 or MgO with MCrAlY or NiAl based bondcoats. This combination also provides hot corrosion and oxidation protection. Erosion protection is obtained using Al_2O_3 and carbide mixtures such as $Ni/WTiC_2$ and $NiCr/Cr_3C_2$/25/.

It is evident from the variety of coating types and methods of applying coatings that the development of turbine coatings has been a large and complex undertaking. Many of the earlier developments directed towards aero turbines are

being applied to land based turbines and coating distinctions between the two types of turbines is becoming nonexistent. The following chronological listing provides a historical perspective of coating development.

1950	Al_2O_3/Al on Ni/Cr alloy aero turbine blades by hot dip aluminizing.
1957	Al_2O_3 on Co based alloy on aero turbine blades by pack cementation.
1960	Al_2O_3 on Ni superalloys IN-713, IN-100, B 1900, aluminide coatings developed for marine gas turbines.
1965	Chromized nickel alloys on land based turbines.
1965	Ceramic thermal barrier coatings applied to rockets and gas turbine sheet metal combustor components.
1968	MCrAlY on nickel alloys for jet turbines by electron beam evaporation.
1970	Al_2O_3/Cr oxide on nickel alloys.
1970	Siliconizing nickel alloys on land based turbines.
1970	Metallic bond coat (NiCr-Al based) and ceramic thermal barrier coating (ZrO_2 based) for gas turbine burners on aero turbines.
1975	MCrAl X X' X^* for low temperature sulphate hot corrosion.
1975	Ni-Cr-Si on nickel alloy for land based turbines.
1975	Aluminide/platinum coatings for oxygen and sulphate hot corrosion on land based turbines.
1975	Beginning of vacuum plasma spraying of turbine components.
1976	Metallic bond coat and ceramic thermal barrier extended to blade coating on aero turbines which resulted in selection of MCrAlY bond coat plus $ZrO_2.8Y_2O_3$ thermal barrier as most suitable but limited use due to corrosion problems by sulphate/vanadium hot corrosion of thermal barrier.
1978	Si_3N_4 on turbine blades by CVD.
1979	Silicon coatings by CVD process of hydrogen reduction of $SiCl_4$ on IN-738 and other high temperature alloys.
1981	Low pressure plasma spraying used to apply MCrAlY coatings.

5.2.1 ***Thermal Barrier Coatings***

Thermal barrier coatings (TBC) are primarily applied to combustion turbine parts of aero engines so that operating temperatures can be increased. This in turn means that the machine will operate more efficiently providing financial gains. It is feasible that with thermal barrier coatings and cooling, utility combustion turbines may be able to operate at temperatures well in excess of the superalloy melting temperatures. Thermal barrier coatings are typically based on stabilized zirconium oxide. The available information on these coatings is not exhaustive and the qualitative nature only allows making estimates of metal temperature reduction and design methods for components.

Ceramic coatings as thermal barriers were used in the 1960 s to protect aero turbine combustion section sheet metal parts with developmental use extended to the turbine section in the 1970's. To date, this technology has developed to the point that its use is made in all types of turbines and diesels. The term thermal barrier usually covers all the layers of the coating system, as these coatings always consist of at least two separate layers, the metallic bond coat and covering ceramic/oxide. The most widely used thermal barrier coating system for utility turbines is an MCrAlY (NiCrAlY or NiCoCrAlY) metallic bond coat with a ceramic zirconia (ZrO_2 + Y_2O_3 or ZrO_2 + MgO) thermal barrier coat. Thicker thermal barrier coatings are often applied using multi-source evaporation, sputtering or ion plating in order to get a graded concentration change from the metal to the oxide. This enhances the ability of the coating to withstand thermal stresses during temperature cycles.

In the MCrAlY-ZrO_2 TBC system, cracks are often present in the ZrO_2 layer which could propagate into the blade material if not for the crack arresting ability of the ductile MCrAlY. The coatings are not very thick, typically in the range of 0.15 to 0.20 mm for the metal basecoat and 0.1 to 0.3 mm for the ceramic layer. The crack arresting capability of TBC is critical as one of the major life extending functions of these coatings is to reduce thermal stresses in blades which reduces low cycle thermal fatigue damage. A properly functioning TBC can have a temperature gradient across it of several hundred degrees centigrade which relieves the superalloy of having to bear a significant cycling temperature gradient. A large reduction in the metal temperature also significantly reduces the amount of creep which would take place in a blade when compared with a simple metallic coating.

The most commonly used technique to apply TBC in the recent past has been plasma spraying which can produce temperatures well in excess of the 2715°C melting point of zirconia. Adhesion of the ceramic to the metallic bondcoat is primarily by a "keying" mechanism rather than atomic bonding. Zirconia and the bondcoat can also be produced by PVD which results in smoother coatings. Adhesion in this case is enhanced by interdiffusion and there is less of a "keying" effect.

Magnesia and yttria are added to zirconia to stabilize phases which prevent the catastrophic tetragonal to monoclinic phase change at around 1,000°C. Magnesia stabilizes the high temperature cubic zirconia phase quenched during plasma spraying but temperatures above 950°C cause a gradual change to the monoclinic form. This transformation increases the thermal conductivity of the coating and if held at elevated temperatures long enough, will subsequently transform to the undesirable tetragonal zirconia.

With 8% yttria a metastable, shear transformation, tetragonal phase is formed which is reasonably stable from room temperature to 1400°C. Since the 8% yttria stabilized zirconia has such high stability and doesn't involve any phase transformation during temperature cycling, it is the preferred stabilizer for the zirconia TBC system. A potential problem which has not been fully explored is the leaching and volatilization of the yttrium stabilizer by fuel contaminants.

The basic MCrAlY bondcoats have been modified primarily on a trial and error basis to improve specific properties. This has resulted in various levels of the major metallic components and a variety of modifier elements all of which can be generally described by the formula $MCr_yAl_zXX'X"...$ where the X's represent modifiers such as yttrium, hafnium and platinum.

6.0 *PERFORMANCE EXPERIENCE AND REQUIREMENTS OF COATINGS*

Although much of the experience and findings which exist for aero turbines is applicable to industrial coatings, differences nevertheless exist. The operating conditions and design requirements for industrial turbines can be significantly different from those of aero turbines. Industrial turbines use a variety of fuels and are expected to operate for at least several tens of thousands of hours before any maintenance. Industrial turbines can also be expected to operate at various duty levels which results in unpredictable stop/start occurrences and varying load factors which will affect the turbine temperature distribution. A coating can potentially be tailored to very specific operating conditions but if this changes, problems may arise. It may therefore be more prudent to use a coating which will afford reasonable protection for all anticipated operating conditions.

The service life of a coating will be a function of its ability to withstand chemical attack and mechanical effects or a combination of the two. The severity of these destructive mechanisms will be determined by the following operating factors:

i) fuel
ii) air quality
iii) treatment of working gases
iv) temperature of operation
v) temperature cycling
vi) turbine cycling

A general discussion reviewing and drawing conclusions from the operating experience of coatings is difficult since so many different types of coatings exist which are used under widely varying conditions on different substrates. The most suitable method to discuss experimental and operational experience, which is usually followed by those working in the field, is by coating type/19/. This categorization method can be summarized as the following:

1. chromium based coatings
2. aluminum based coatings
3. silicon based coatings
4. NiCrSi compound coatings
5. MCrAlY coatings
6. oxide/ceramic coatings

A limited review of the operating/experimental experience of various coating systems was undertaken with the results tabulated in Tables 9A to 9F.

Chromium coatings were initially viewed as a suitable choice to protect land based turbine components since the superalloys employed had low chromium contents. The philosophy was that low chromium content, γ' strengthened nickel superalloys could function with good high temperature strength while a high chromium content coating would provide the necessary high temperature environmental protection. Some of the reported performance characteristics are provided in Table 9A. On IN-738 LC vanes, the chromium diffusion coating was found to spall and exfoliate in industrial air.

Aluminum diffusion coatings have been generally found to reduce the creep strength of various high temperature alloys as summarized in Table 9B. When modified by platinum, creep strength was not a problem but hot corrosion and oxidation became life limiting influences. As indicated in Table 9D, the diffusion zone appears to be where the problem originates. Silicon coatings have been found to form brittle silicides and reduce the creep properties of superalloys as indicated in Table 9C. Satisfactory performance appears possible with NiCrSi although as indicated in Table 3E, aluminum diffusion into the coating from the substrate can reduce hot corrosion resistance.

As indicated in Table 9F, MCrAlY coatings can be degraded by Type II hot corrosion mechanisms although it is resistant to Type I hot corrosion. The success of this type of coating is dependent on the operating history of the turbine which can prevent undesirable temperature variations resulting in hot corrosion.

Although much progress has taken place in the development of TBC technology in the last decade, significant areas of performance are still not well understood. Some of these time-temperature dependent characteristics include fatigue, creep, phase changes and sintering. In isothermal testing, it has been found that TBC can withstand any expected temperature gradient in combustion turbines without cracking. Cracking does take place in turbines which indicates sources of cyclic stresses are important to understanding the ultimate failure mode.

Thermal barrier coatings have not reached a degree of development where their application in the turbine section is universally accepted and they are most often found in the advanced, high temperature turbines. A 0.13 mm thick TBC can

reduce the surface temperature of a turbine blade by almost 200°C/27/. This allows the turbine to operate at higher firing temperature or reducing internal blade cooling which can significantly increase efficiency.

At temperatures above 850°C, it has been found that MCrAlY bondcoats can creep significantly and in some cases lead to coating failure. However, it is likely that this property also relieves the thermal stresses which develop during heating and prevents the ceramic coating from spalling off. The bondcoat must possess an optimal creep level to provide the best service characteristics. It must also be recognized that oxidation and other structure changing mechanisms can take place with time in the bondcoat, reducing the coating's ability to minimize thermal stress effects caused by creep. When this point is reached, spalling of the ceramic layer takes place requiring repair. The ceramic coating typically develops cracks through the coating but these do not lead to the failure. It is not until biaxial compressive stresses in the ceramic produce tensile stresses perpendicular to the coating that delamination takes place/28/. The delamination results in failure since that area of the coating reaches the gas temperature due to insufficient cooling and the resulting stresses tear off the coating. These failures of the ceramic coating have been found to take place within the ceramic adjacent to the ceramic/bondcoat interface. This finding would tend to support the conclusion that to avoid failures it is more important to control how the interface transmits stresses rather than the level of adhesion of the interface.

Failure of TBC can also result due to excessive oxidation of the bondcoat by either a gaseous route through cracks or by ionic transport through the lattice of the zirconia. The sound ceramic does however, provide oxidation protection by lowering the temperature and oxygen partial pressure at the bondcoat. The TBC can also degrade γ' strengthened substrates by having aluminum diffuse into the bondcoat dissolving γ' precipitates and forming titanium carbides at the grain boundaries/28/.

7.0 *NECESSARY RESEARCH AND DEVELOPMENT*

From the foregoing it is clear that gas turbine manufacturers recognize that considerable development effort will be required to adapt the most recent aircraft engine hot section technology to the larger component size and greater life expectancies required in industrial land-based units. It would be both impractical and inappropriate for Ontario Hydro to attempt such work either in parallel or in competition with major equipment suppliers. However, we should position ourselves as informed prospective buyers and operators of large industrial combustion turbine and I.G.C.C. generating plant. To this end, in the area of coated superalloy technology a vast spectrum of activities could be undertaken. These must however be consistent with the level of available resources, the resource capabilities and the expected beneficial impact on the combustion turbine program. Consequently, choices must be made to select a focused program which has a high probability of realizing benefits. The following are some goals formulated in the Materials Technology Section:

a) Typical gas turbine combustor sheet, cast turbine section stationary vane and both cast and forged airfoil materials should be obtained with coatings of the aluminide, M-Cr-Al-Y and stabilized zirconia types. It is desirable to test coatings applied by the pack cementation, physical vapour deposition and thermal spray methods. Selected samples should receive the benefit of laser surface modification.

b) The test program should involve base line creep and fatigue testing of both coated and uncoated material together with microstructural examination. Coated samples should then be subjected to simulated service conditions in a test rig designed to impose combined creep and low cycle

thermal fatigue stresses in a realistic combustion environment. Following the rig exposure, the base line tests would be repeated to assess both the degree of material degradation and the relative merits of the candidate substrates and coatings.

c) In addition to tests on commercially available coatings it is expected that in-house plasma sprayed and laser modified formulations would be developed for testing. The Chemical Research Department have agreed to cooperate in the design of combustion equipment and fuel specifications for the test program. It is anticipated that natural gas firing will be superseded at a later date by gas from a coal gasifier. Tests should utilize gas of both normal and off-specification conditions.

Figure 6 provides a schematic representation of the capabilities to be developed at Research Division as well as the expected objectives which will benefit the corporate programs involving combination turbines.

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TABLE 1
COMPOSITION OF COMPRESSOR MATERIALS

	ELEMENT: Wt% CONCENTRATION										
COMPONENT	C	Mn	Si	S	P	Cr	Ni	Mo	Nb	Cu	N
1&2 ASTM spec. A217 gr. CA 15.	0.15 max.	1.00 max.	1.5 max.	0.04 max.	0.04 max.	11.5-14.0	1.0 max.	0.5 max.	-	-	-
ASTM spec. A747 gr. CB7 Cu-1	0.07 max.	0.70 max.	1.0 max.	0.03 max.	0.03 max.	15.5-17.7	3.6-4.6	-	0.15-0.35	2.5-3.2	0.05 max.
3&4 ASTM spec. A473 type 403.	0.15 max.	1.00 max.	0.5 max.	0.03 max.	0.04 max.	11.5-13.0	-	-	-	-	-
ASTM spec. A705 type 630	0.07 max.	1.00 max.	1.0 max.	0.03 max.	0.04 max.	15.0-17.5	3.0-5.0	-	-	3.0-5.0	-
5 ASTM spec. A471 Class 9	0.28 max.	0.70 max.	0.1 max.	0.01 max.	0.01 max.	0.75-2.0	2.0-4.0	0.2-0.7	V 0.05-min.	-	-
ASTM spec. A565 gr 616	0.20-0.25	0.5-1.0	0.5 max.	0.02 max.	0.02 max.	11.0-12.5	0.5-1.0	0.9-1.25	0.2-0.3	W 0.9-1.25	-
6 ASTM spec. A278 Class 70	3.8* max.	-	-	0.12	0.25	-	-	-	-	-	-
ASTM spec. A356 gr. 1	0.35 max.	0.7 max.	0.6 max.	0.03 max.	0.035 max.	-	-	-	-	-	-
ASTM spec. A515 gr. 70	0.35 max.	1.3 max.	0.13-0.45	0.04 max.	0.035 max.	-	-	-	-	-	-

*Carbon Equivalent = Wt %C + 0.3 (Wt.%Si + Wt.%P)
Components 1 & 2: Cast compressor blades and vanes.
Components 3 & 4: Forged compressor blades and vanes.
Component 5 : Forged compressor discs.
Component 6 : Cast or weld fabricated compressor casings.

TABLE 2

MECHANICAL PROPERTIES OF COMPRESSOR MATERIALS

COMPONENTS	*UTS MPa*	*0.2% P.S. MPa*	*%El. ON 4D*	*% RA*
1&2 ASTM spec. A217 gr. CA15. ASTM spec. A747 gr. CB7 Cu-1 (H1100)	620- 795 930 min.	450 min. 760 min.	18 min. 9 min.	30 min. -
3&4 ASTM spec. A473 type 403 ASTM spec. A705 type 630 (H1100)	485 min. 965 min.	275 min. 793 min.	20 min. 14 min.	45 min. 45 min.
5 ASTM spec. A471 Class 9 ASTM spec. A565 Gr. 616 (HT)	1170 min. 965 min.	1070- 1205 760 min.	12 min. 13 min.	35 min. 30 min.
6 ASTM spec. A278 Class 70 ASTM spec. A356 Gr. 1 ASTM spec. A515 Gr. 70	483 min. 485 min. 485- 620	- 250 min. 260 min.	- 20 min. 21 min.	- 35 min. -

TABLE 3

COMPOSITION OF COMBUSTION ZONE MATERIALS

	ELEMENT: Wt% CONCENTRATION						
ALLOY TYPE	*C*	*Mn*	*Si*	*Cr*	*Ni*	*Mo*	*OTHERS*
Solid soln. +carbide dispersion strengthening (Haynes 188)	0.01	1.25	0.35	22	22	-	W: 14, Co: 37.25 Fe: 3, La: 0.5
Solid soln. + gamma prime dispersion strengthening (Nimonic 263)	0.06	-	-	20	50.74	5.9	Ti: 2.15, Co: 20, Al: 0.45, Fe: 0.7
Solid soln. Strengthening (Nimonic 86)	0.05	-	-	25	64.9	10	Mg: 0.015, Ce: 0.03
ASTM spec. A351 gr. CK20	0.20 max.	1.5 max.	1.75 max.	23-27	19-22	-	
Oxide dispersion strengthening (Incoloy MA 956)	-	-	-	20	Bal.		Al: 5, Y_2O_3: 0.5
ASTM Spec. A356 Gr. 10	0.20 max.	0.5-0.8	0.6 max.	2.0-2.75	-	0.9-1.2	S: 0.03 max P: 0.035 max
ASTM spec. A387 Gr. 22	0.15 max	0.25-0.66	0.5 max.	1.88-2.62	0.85-1.15	-	S: 0.035 max P: 0.035 max

TABLE 4

MECHANICAL PROPERTIES OF COMBUSTION ZONE MATERIALS

ALLOY	*0.2% P.S. MPa*	*1000 HR. RUPTURE STRESS AT 870°C MPa*	*OXIDATION mm/SIDE**
Haynes 188	500	70	0.06
Nimonic 263	600	50	0.38
Nimonic 86	400	50	0.13
CK 20	195	-	0.13
MA-956	500	100	0.005
A356 Gr. 10	380	-	-
A387 Gr. 22	310	-	-

* After 400 cycles involving heating to 1100°C in one minute, holding for thirty minutes and cooling to 350°C in one minute.

TABLE 5

COMPOSITION OF TURBINE SECTION MATERIALS

	ELEMENT Wt% CONCENTRATION									
COMPONENT	**C**	**Fe**	**Ta**	**B**	**Cr**	**Ni**	**Co**	**W**	**Al**	**OTHERS**
1. (X-45) (ECY-768)	0.25 0.60	2.0 1.0	- 3.5	0.01 0.01	25 23.5	10.5 10.0	Bal. Bal.	7 7	- 0.15	- -
2. Cast (IN-738) Forged (U-520)	0.10 0.05	-	1.75 -	0.01 0.005	16 19	Bal Bal	8.5 12	2.6 1	3.4 2	Zr: 0.05 Mo: 1.75 Nb: 0.9 Mo: 6 Ti: 3
Cast Single Crystal (PWA 1480)	-	1.5	12	-	10	Bal	5	4	5	-
Cast Direc-tionally Solidified (MAR-M-247)	-	1.0	3	0.015	8.2	Bal	10	10	5.5	Zr: 0.05 Hf: 1.5
1&2 Oxide Dispersion Strengthened (MA-6000)	0.15	2.5	-	0.01	15	Bal	-	4	4.5	Zr: 2 Mo: 2 Hf: 2 Y_2O_3: 2.5
3 (M-152) ASTM spec. A565 Gr. XM-32	0.12 0.08- 0.15	- -	- -	- -	12 11- 12.5	2.5 2.0- 3.0	Bal Bal	- -	- -	V: 0.3 Mo: 2 Mn: 0.7 Mn: 0.5-0.9 V: 0.25-0.4 Si: 0.35 max S: 0.025 max P: 0.025 max

Component 1 = Cast stationary vanes
Component 2 = Cast and forged airfoils
Component 3 = Forged discs

TABLE 6

MECHANICAL PROPERTIES OF TURBINE SECTION MATERIALS

ALLOY	*RUPTURE STRESS AT 870°C*
X-45	76 (1)
ECY-768	166 (1)
U-520	159 (1)
PWA-1480	300 (2)
MAR-M-247	230 (2)
MA 6000*	230 (2)
M-152	-
XM-32	-

(1) Stress for rupture in 1000 hours
(2) Stress for rupture in 10,000 hours

* At temperatures above 900°C oxide dispersion strengthened alloys have far superior stress rupture properties when compared with the other listed materials.

TABLE 7

COATING CATEGORIZATION BASED ON MECHANISM RESPONSIBLE FOR COATING APPLICATION

	COATING APPLICATION MECHANISM						
	PHYSICAL	*CHEMICAL*	*ELECTROCHEMICAL*	*THERMAL SPRAYING*	*MECHANICAL*	*WELD OVERLAYING*	*OTHER INDIVIDUAL CATEGORIES*
Specific Types of Coating Processes	· Sputter · Evaporation · Ion plating	· Pack cementation · Electroless	· Aqueous · Fused Salt	· Detonation gun · Flame · Electron arc · Plasma	· Cladding · Bonding	· SMAW · MIG · TIG · PAW transferred arc · PAW nontransferred arc · Submerged arc	· Ion implantation · Laser modification · Hot dip coating

SMAW: Shielded Metal-Arc Welding
MIG: Gas Metal Arc Welding
TIG: Gas Tungsten-Arc Welding also identified by GTAW acronym
PAW: Plasma-arc Welding

91-65

TABLE 8

CHARACTERISTICS OF EVAPORATION COATING TECHNIQUES

METHOD	*DIRECT EVAPORATION*		*GAS SCATTERING EVAPORATION*	
TYPE	*VACUUM EVAPORATION*	*ACTIVATED EVAPORATION*	*REACTIVE EVAPORATION*	*ACTIVATED REACTIVE EVAPORATION (ARE)*
Coatings produced	Single elements; alloys	Alloys; compounds	Compounds	Refractory Compounds
Evaporation source	Any suitable source Single source for elements or alloys; wire or rod feed. Multiple source for alloys - but with reduced deposition rate.	Any source; usually electron beam.	Usually electron beam	Usually electron beam
Atmosphere	Vacuum	Plasma	Reaction gas	Reactive gas & plasma
Substrate Electrical State		Floating, Grounded or electrically biased	Floating, Grounded or electrically biased	Biased ARE (BARE): Substrate is -ve biased; also called Reactive Ion Plating (RIP). Enhanced ARE (EARE): Uses a thermionic electron emitter together with electron beam heating

TABLE 9A

SUMMARY OF REPORTED PERFORMANCE CHARACTERISTICS OF CHROMIUM COATINGS

TYPE OF COATING	SUBSTRATE	FUEL	PERFORMANCE CHARACTERISTICS	CORRECTIVE ACTION TO PERFORMANCE PROBLEMS	REFERENCE
CHROMIUM					
Cr Diffusion	Udimet 520	Natural gas with H_2S	-satisfactory after 2000 hours at 650-850°C	-	32 (Schmitz)
Cr Diffusion (BBC BG24 Coating)	Austenitic SS blades	Blast furnace gas turbine	-satisfactory after 25,000 hours	-	33 (Bauer)
Cr Diffusion (BBC BG24 Coating)	Austenitic SS blades	Crude oil gas turbine	-satisfactory after 95,000 hours	-	19 (Burgel)
Cr Diffusion (BBC DP24 Coating)	Nimonic 80 A vanes	-	-satisfactory after 35,000 hours at 710 -730°C	-	33 (Bauer)
Cr Diffusion (BBC BG24 Coating)	IN-738 LC vanes	Gas turbine	-severe spalling and exfoliation after 12,500 hours -highly industrial air with gas inlet temperature of 820°C	-switched to NiCrSi overlay	33 (Bauer)

TABLE 9B

SUMMARY OF REPORTED PERFORMANCE CHARACTERISTICS OF ALUMINUM COATINGS

TYPE OF COATING	*SUBSTRATE*	*FUEL*	*PERFORMANCE CHARACTERISTICS*	*CORRECTIVE ACTION TO PERFORMANCE PROBLEMS*	*REFERENCE*
ALUMINUM					
Al-Cr Duplex (pack cementation)	Udimet 520	Air testing	-loss of creep strength and ductility at 802°C due to decarburization of grain boundaries	-remove grain boundary effects with single crystals	20 (Castillo)
Al Diffusion (pack cementation)	IN-738 ECY-768	Rig testing	-loss of tensile and stress rupture properties at high temp.	-	20 (Mazzei by Castillo)
Al Diffusion	Nimonic 105	Rig testing	-enhanced corrosion of coating-substrate interface by sulphur compounds, localized attack	- prevent intermetallic formation	14 (Felix)
Al Diffusion (pack cementation)	IN-100	Rig Testing jet fuel	-reduced creep life at 950°C likely due to surface defects which are initiated by corrosion	-no reduction in creep life if chrome-aluminizing is used	21 (Betz)

TABLE 9C

SUMMARY OF REPORTED PERFORMANCE CHARACTERISTICS OF SILICON COATINGS

TYPE OF COATING	SUBSTRATE	FUEL	PERFORMANCE CHARACTERISTICS	CORRECTIVE ACTION TO PERFORMANCE PROBLEMS	REFERENCE
SILICON					
Silicon Diffusion (CVD)	IN-738 LC	-	-loss of rupture life by up to 60% of uncoated	-control post-coating heat treatments	14 (Felix)
Silicon Diffusion (CVD)	Superalloy	-	-corrosion following impact damage of regions with brittle silicides	-	14 (Felix)

TABLE 9D

SUMMARY OF REPORTED PERFORMANCE CHARACTERISTICS OF PLATINUM MODIFIED ALUMINIUM COATINGS

TYPE OF COATING	*SUBSTRATE*	*FUEL*	*PERFORMANCE CHARACTERISTICS*	*CORRECTIVE ACTION TO PERFORMANCE PROBLEMS*	*REFERENCE*
Pt-Al					
Pt-Al (T/DEW RT22 diffusion coating)	IN-738 LC first stage blades	clean gas	-satisfactory after 32,000 hrs at 800 °C in industrial environment -thick oxide develops which could possibly spall	-	19 (Burgel)
Pt-Al (T/DEW RT22 diffusion coating)	IN-738 LC first stage vanes	clean gas	-degraded by low temperature, Type II hot corrosion	-Cr_2O_3 oxides would provide greater protection than Al_2O_3 -unacceptable performance	19 (Burgel)
Pt-Al (GE LDC2 diffusion coating)	IN-738 first stage blades	sour gas (>3% H_3S)	-diffusion zone attacked after 35,000 hrs at 700 to 830°C -diffusion zone became nickel rich with low corrosion resistance	-	34 (Wood)
Pt-Rh-Al (diffusion coating)	ECY-768 first stage vanes	Sour gas	-diffusion zone attacked after 15,500 hrs at about 760°C	-unacceptable performance	35 (Spengler)
Pt-Rh-Al (diffusion coating)	X-45 second row vanes	Sour gas	-degraded by internal & surface oxidation after 20,000 hrs	-unacceptable performance	35 (Spengler)

TABLE 9E

SUMMARY OF REPORTED PERFORMANCE CHARACTERISTICS OF NiCrSi COATINGS

TYPE OF COATING	*SUBSTRATE*	*FUEL*	*PERFORMANCE CHARACTERISTICS*	*CORRECTIVE ACTION TO PERFORMANCE PROBLEMS*	*REFERENCE*
NiCrSi					
NiCrSi (plasma)	IN-713 LC first stage vanes	not given	-blisters after 5000 hrs due to Al diffusion into coating reducing sulphate hot corrosion resistance	-lower substrate Al content (ie, 6% to 3.4%) by using IN-738 LC	14 (Felix)
NiCrSi (plasma)	IN-738 LC first stage vanes	not given	-satisfactory after 20,000 hrs	-	14 (Felix)
NiCrSi (APS)	IN-738 LC first stage blades	clean gas	-satisfactory after 32,000 hrs at 800°C in industrial environment -developed thick oxide and Cr depletion	-spalling may be life limiting with frequent stop/starts	33 (Bauer)

TABLE 9F

SUMMARY OF REPORTED PERFORMANCE CHARACTERISTICS OF MCrAlY COATINGS

TYPE OF COATING	*SUBSTRATE*	*FUEL*	*PERFORMANCE CHARACTERISTICS*	*CORRECTIVE ACTION TO PERFORMANCE PROBLEMS*	*REFERENCE*
MCrAlY					
Co-30Cr-5Al-0.5Y (AT ATD14 EB PVD coating)	IN-738 LC first stage vanes	sour gas	-completely degraded after 32,000 hrs at ~800°C by Type II hot corrosion -oxidation of interface	-unacceptable performance	19 (Burgel)
Co-23Cr-12Al-0.35Y (AT ATD2 EB PVD coating)	IN-738 LV first stage vanes	clean gas	- some localized Type II hot corrosion at cooler areas after 32,000 hrs at ~800°C	-recoating necessary	19 (Burgel)
Ni-40Cr-5Al-0.4Y (AT ATD15 EB PVD coating)	IN-738 LC first stage vanes	clean gas	-coating destroyed in many areas with loss of substrate by oxidation and Type II hot corrosion -thick oxide with sulphide front developed	-unacceptable performance	19 (Burgel)
Co-22Cr-1341-1Y (EB PVD coating)	IN-738 LC first stage blades	sour gas	-coating destroyed by either corrosion or erosion after 35,000 hrs -processing defects prone to attack.	-	34 (Wood)
Co-22Cr-13Al-1Y (VPS coating)	IN-738 LC fist stage blades	sour gas	-coating destroyed by either corrosion or erosion after 35,000 hrs -processing defects led to attack	-unacceptable performance due to poor coating quality (pre 1980 plasma spraying)	19 (Burgel)

SUMMARY OF ACRONYMS FOR TABLE 9

APS - Air Plasma Spraying

AT - Airco Temescal

BBC - Brown Boveri Company

GE - General Electric

PVD - Physical Vapour Deposition

T/DEW - Thyssen/Deutsche Edelstahlwerke

VPS - Vacuum Plasma Spraying

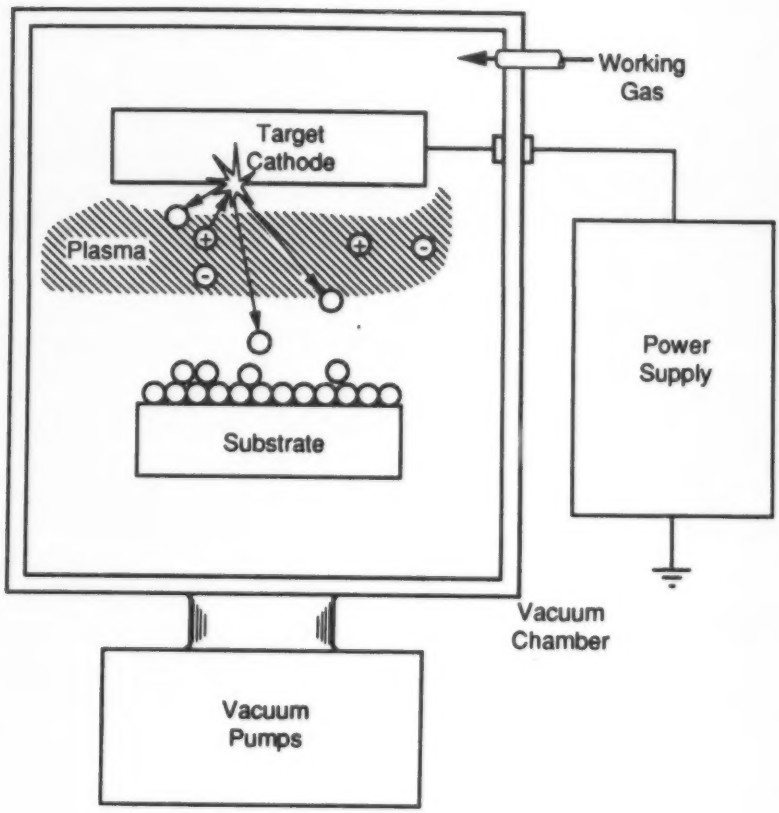

FIGURE 1

SPUTTER DEPOSITION PROCESS

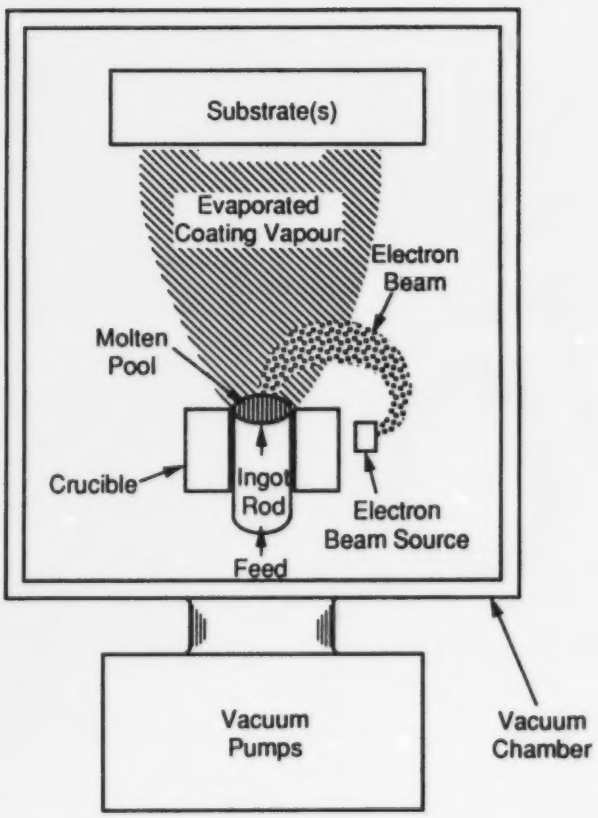

FIGURE 2

ELECTRON BEAM VACUUM EVAPORATION PROCESS

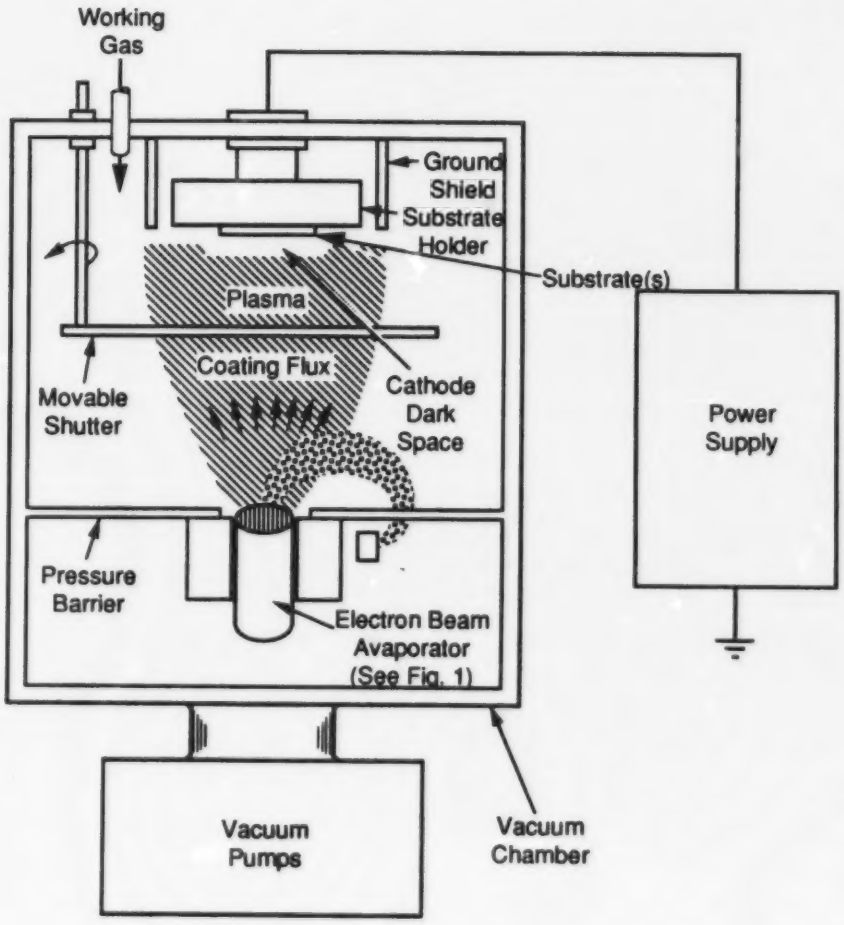

FIGURE 3

ION PLATING PROCESS

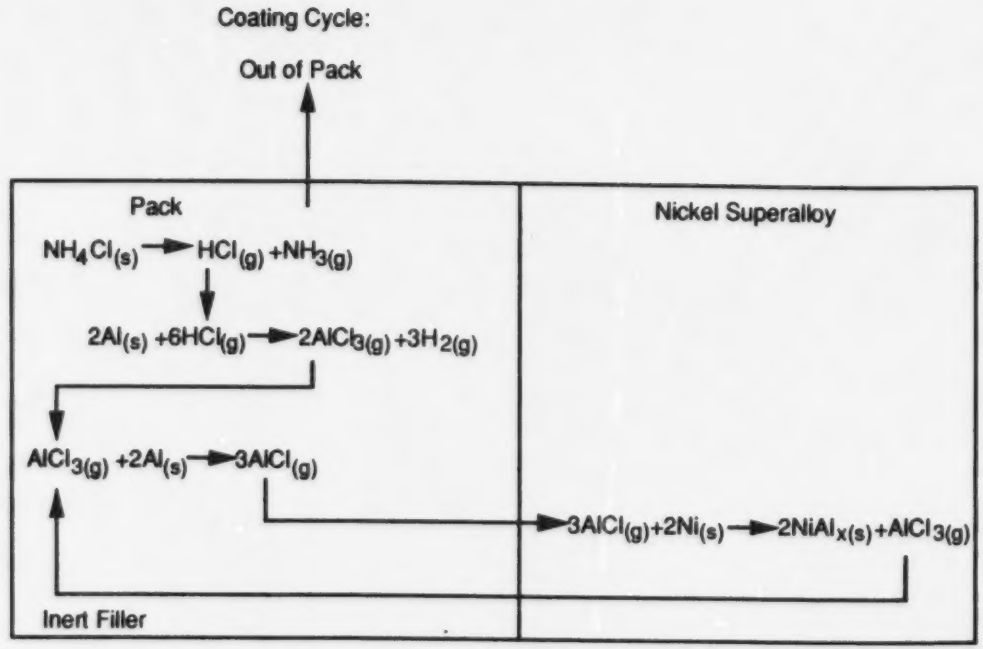

FIGURE 4

PACK CEMENTATION PROCESS OPERATING SEQUENCE AND COATING CYCLE REACTIONS

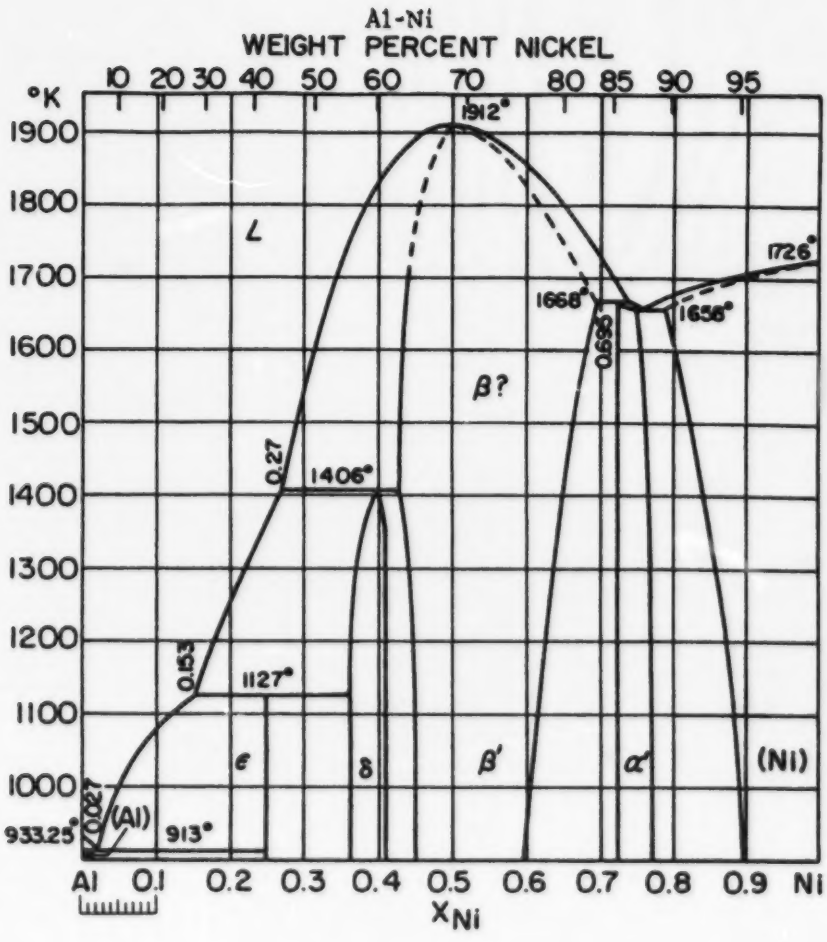

FIGURE 5

ALUMINUM - NICKEL EQUILIBRIUM PHASE DIAGRAM

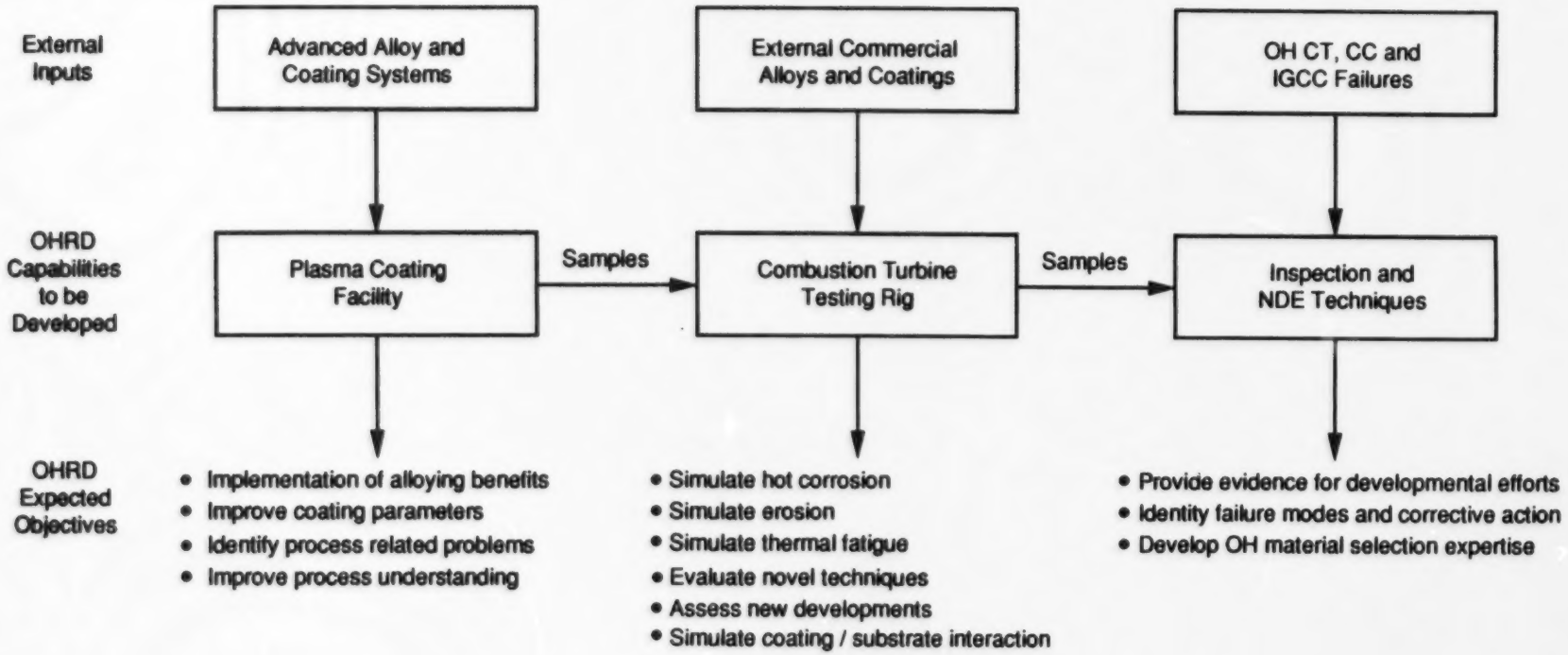
External Inputs
Advanced Alloy and Coating Systems
External Commercial Alloys and Coatings
OH CT, CC and IGCC Failures
OHRD Capabilities to be Developed
Plasma Coating Facility
Samples
Combustion Turbine Testing Rig
Samples
Inspection and NDE Techniques
OHRD Expected Objectives
• Implementation of alloying benefits
• Improve coating parameters
• Identify process related problems
• Improve process understanding
• Simulate hot corrosion
• Simulate erosion
• Simulate thermal fatigue
• Evaluate novel techniques
• Assess new developments
• Simulate coating / substrate interaction
• Provide evidence for developmental efforts
• Identity failure modes and corrective action
• Develop OH material selection expertise

FIGURE 6

OHRD COMBUSTION TURBINE AND HIGH TEMPERATURE MATERIALS DEVELOPMENTAL PROGRAM

91-65 185545-AF43-RD